



Effects of Doping and/or Atmosphere on the Electrical Conductivity of $\text{Li}_4\text{Ti}_5\text{O}_{12}$

**by Jeff Wolfenstine, Donald Foster, Jeffrey Read, Shengshui Zhang,
and Jan L. Allen**

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Sensors and Electron Devices Directorate, ARL

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14. ABSTRACT <p>Tantalum (Ta) doping in lithium titanium oxide, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ ($\text{Li}_4\text{Ti}_{4.95}\text{Ta}_{0.05}\text{O}_{12}$), as function of different heat-treatment atmospheres (oxidizing/reducing) was investigated and compared to $\text{Li}_4\text{Ti}_5\text{O}_{12}$ to determine its effect on electrical conductivity and rate capability. The ionic conductivity value of the white colored $\text{Li}_4\text{Ti}_{4.95}\text{Ta}_{0.05}\text{O}_{12}$ heated under an oxidizing atmosphere was $\sim 3 \times 10^{-8}$ S/cm with a DC electronic conductivity value of $\sim 1 \times 10^{-9}$ S/cm. These values are similar to values observed for $\text{Li}_4\text{Ti}_5\text{O}_{12}$ heated under the same oxidizing atmosphere. These results suggest that both materials are predominately ionic conductors, with the extra charge of Ta compensated by a lattice defect, most likely titanium (Ti) vacancies. For the case of $\text{Li}_4\text{Ti}_{4.95}\text{Ta}_{0.05}\text{O}_{12}$ heated under a reducing atmosphere, it was purple colored with an electronic conductivity value of $\sim 1 \times 10^{-3}$ S/cm. $\text{Li}_4\text{Ti}_5\text{O}_{12}$ heated under a reducing atmosphere was also purple colored with an electronic conductivity value of $\sim 3 \times 10^{-5}$ S/cm. These results suggest both of these materials are predominately electronic conductors where the electronic conductivity is a result of the reduction of some Ti^{+4} ions into Ti^{+3} ions. For $\text{Li}_4\text{Ti}_{4.95}\text{Ta}_{0.05}\text{O}_{12}$ this reduction is a result of the extra charge of the Ta whereas for $\text{Li}_4\text{Ti}_5\text{O}_{12}$ it is a result of nonstoichiometry.</p>				
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1. Introduction

Recently, there has been considerable interest in lithium titanium oxide ($\text{Li}_4\text{Ti}_5\text{O}_{12}$) as a potential anode for use in lithium (Li)-ion batteries (1–5). It has many advantages compared to the currently used graphite. For example, it is a zero-strain Li insertion host suggesting a virtually unlimited cycle life. It features a flat, operating voltage of about 1.5 V versus Li, above the reduction potential of common electrolyte solvents, thus, it does not form a solid electrolyte interface based on solvent reduction, which should be a favorable property for high rate and low temperature operation. However, several disadvantages exist compared to graphite. These include low electronic conductivity. As a result, several methods have been used to increase electronic conductivity with the intent of improving rate-capability. These include forming a composite of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and a conductive second phase (silver (Ag)) (6); doping $\text{Li}_4\text{Ti}_5\text{O}_{12}$ with magnesium (Mg^{+2}) on the Li^+ sites and then heating under reducing conditions (7); and heating pure $\text{Li}_4\text{Ti}_5\text{O}_{12}$ under a reducing atmosphere (8).

Another possibility to increase the electronic conductivity of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is to substitute an M^{+5} ion (i.e., tantalum (Ta^{+5})) on a titanium (Ti^{+4}) site, which should lead to an increase in electron concentration for heat-treatment under reducing conditions. This is according to the charge neutrality condition (Kroger-Vink (9) notation is used) given in equation 1 and hence, an increase in electronic conductivity.

$$[e'] = [\text{Ta}^{\bullet}_{\text{Ti}}] \quad (1)$$

where an electron, e' , corresponds to Ti^{+3} on a Ti^{+4} site.

For the case of oxidizing conditions, the extra charge of Ta should be compensated by lattice defects (9–11). It is likely that charge compensation can be accomplished by either a Li vacancy or a Ti vacancy, as given in equations 2 and 3, respectively. It should be noted that for the case of Li it can sit on tetrahedral and octahedral sites; whereas, Ti sites only on octahedral sites in the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ spinel structure (2, 3, 5).

$$[\text{V}'_{\text{Li}}]_{\text{tetrahedral}} + [\text{V}'_{\text{Li}}]_{\text{octahedral}} = [\text{Ta}^{\bullet}_{\text{Ti}}] \quad (2)$$

$$4 [\text{V}''''_{\text{Ti}}] = [\text{Ta}^{\bullet}_{\text{Ti}}] \quad (3)$$

For the case charge compensation by a Li vacancy, an increase in Li-ion conductivity would be expected compared to undoped $\text{Li}_4\text{Ti}_5\text{O}_{12}$. In this case the defect model is of the form $\text{Li}_{1-x}\text{V}^{\text{Li}}_x[\text{Li}_{1/3-y}\text{V}^{\text{Li}}_y\text{Ti}_{5/3-z}\text{Ta}_z]\text{O}_4$ in spinel notation (2, 5); whereas, for the case of charge compensation by a Ti vacancy, no significant increase in Li-ion ionic conductivity would be expected compared to undoped $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and the defect model is of the form $\text{Li}[\text{Li}_{1/3}\text{Ti}_{5/3-z}\text{Ta}_{z/5}\text{V}^{\text{Ti}}_{4z/5}]\text{O}_4$. Thus, a comparison of the ionic conductivity of Ta doped to undoped $\text{Li}_4\text{Ti}_5\text{O}_{12}$ can be used to determine the charge compensating lattice defect.

It is the purpose of this report to investigate the effects of Ta doping on the ionic/electronic conductivity of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ as a function of heat-treatment atmospheres (reducing and oxidizing conditions) and on the rate-capability. The results will be compared to $\text{Li}_4\text{Ti}_5\text{O}_{12}$ under similar heat-treatment conditions.

2. Experimental

2.1 Materials Preparation

$\text{Li}_4\text{Ti}_5\text{O}_{12}$ samples were prepared using a solid-state method from titanium dioxide (TiO_2) (rutile structure) and lithium carbonate (Li_2CO_3) (12). The Ta doped $\text{Li}_4\text{Ti}_5\text{O}_{12}$ was prepared also using a solid-state method with TiO_2 (rutile structure), Li_2CO_3 , and Ta metal. In both cases three weight percent excess Li_2CO_3 was used to compensate for lithia volatilization during the high temperature heating. A 1% Ta doping level was selected, which yields the following composition, $\text{Li}_4\text{Ti}_{4.95}\text{Ta}_{0.05}\text{O}_{12}$ assuming that Ta sits on a Ti site. This is probably a good assumption in that the volume change is about a factor of ~ 3.8 times greater if Ta^{+5} sits on Li^+ tetrahedral sites and ~ 3.3 times greater if Ta^{+5} sits on Li^+ octahedral sites rather than on Ti^{+4} octahedral sites (13). This Ta doping level was selected because it has been observed that 1% doping of niobium (Nb^{+5}) into TiO_2 increased the electronic conductivity from about $\sim 10^{-13}$ to 10^{-2} S/cm (14). The starting materials were ground with an alumina mortar and pestle with enough methanol to form a slurry. The dried and mixed reactant mixture was pelletized and then heated at 800 °C for 12 h in air (oxidizing) or 3 vol. % hydrogen/argon (H_2/Ar) (reducing). The sample was reground, pelletized, and heated for another 24 h at 800 °C in air or H_2/Ar . The powders were reground and uniaxially pressed into cylindrical specimens 13 mm in diameter with a thickness between 2–4 mm at pressure of 200 MPa. A 5 wt. % polyvinyl alcohol binder was used. The pellets were then sintered at 800 °C for 12 h in air or H_2/Ar .

2.2 Physical Characterization

The density of the sintered pellets was measured using the Archimedes method with methanol as the immersion medium. The samples were characterized by x-ray diffraction. Lattice constants were determined by fitting the data using the Rietveld refinement (15).

2.3 Electrical Conductivity Measurements

DC and AC room temperature conductivity were determined on sintered and polished disk samples using the two probe method. Silver paste electrodes were applied to the top and bottom surfaces of the disk. DC resistances were measured using a Keithly 6517A Electrometer/High Resistance Meter with a Model 8009 Resistivity Test Fixture capable of measuring volume resistivities as high as 10^{18} ohms-cm. High resistance samples required equilibration times of about 18–24 h to ensure steady-state was achieved. AC impedance was measured using a Solatron 1260 Impedance Analyzer in the frequency range 1 to 10^6 Hz.

3. Results and Discussion

3.1 Materials

Both $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and $\text{Li}_4\text{Ti}_{4.95}\text{Ta}_{0.05}\text{O}_{12}$ samples that were heated under air were white colored, indicative of an electronic insulator; whereas, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and $\text{Li}_4\text{Ti}_{4.95}\text{Ta}_{0.05}\text{O}_{12}$ samples heated under H_2/Ar were purple colored. Previous results (8) based on x-ray photoelectron spectroscopy had shown that the color change from white to purple for $\text{Li}_4\text{Ti}_5\text{O}_{12}$ was a result of some of the Ti^{+4} ions being reduced to Ti^{+3} ions during heat-treatment under reducing conditions.

The x-ray diffraction (XRD) pattern(s) of $\text{Li}_4\text{Ti}_{4.95}\text{Ta}_{0.05}\text{O}_{12}$ heated under air or H_2/Ar are shown in figure 1. From figure 1 it can be observed that the patterns for $\text{Li}_4\text{Ti}_5\text{O}_{12}$ heated under air or H_2/Ar are similar. They both represent a single-phase cubic material with an $\text{Fd}3\text{m}$ space group.

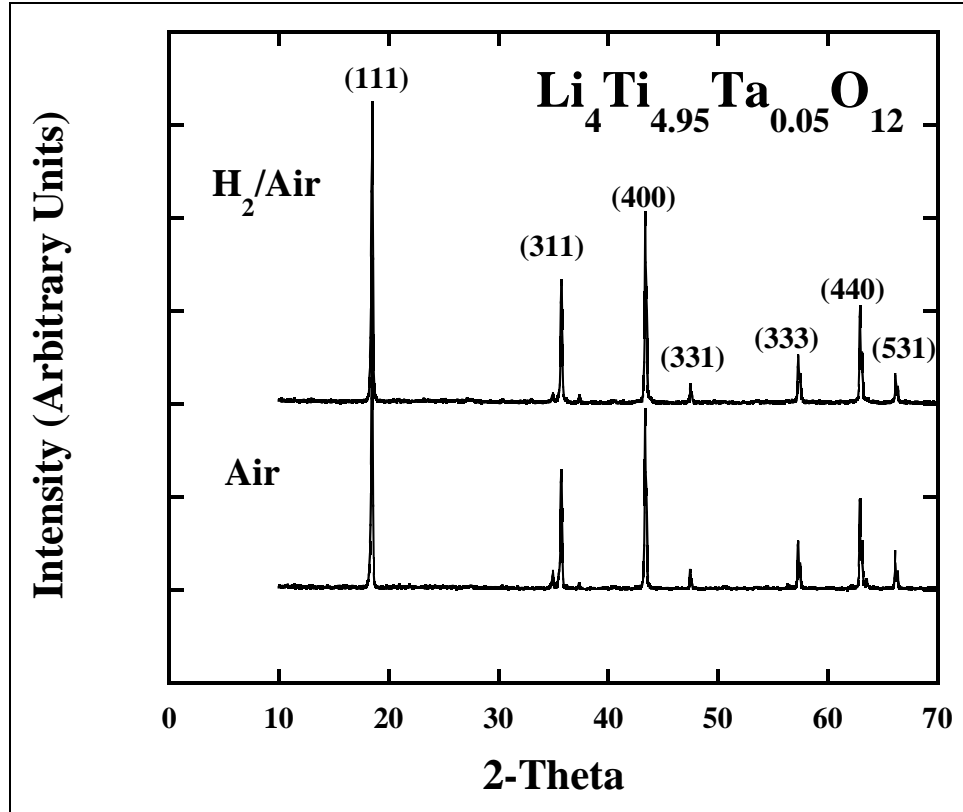


Figure 1. XRD pattern of $\text{Li}_4\text{Ti}_{4.95}\text{Ta}_{0.05}\text{O}_{12}$ synthesized under air or 3 vol. % H_2/Ar .

3.2 Electrical Conductivity

The room temperature AC conductivity results for $\text{Li}_4\text{Ti}_{4.95}\text{Ta}_{0.05}\text{O}_{12}$ heated under air using Li-ion blocking Ag electrodes are shown in the complex impedance plot in figure 2. From figure 2 several important points are observed. Firstly, the data separates into a high frequency region, which contains a semicircle, and low frequency region, which contains a spike. For this case,

since we have Li blocking electrodes the shape of the curve represents a material that is predominately a Li-ion conductor with very low electronic conductivity (16–19). Secondly, the low frequency intercept of the semicircle on the Z' axis gives the total ionic resistance, which for the case of $\text{Li}_4\text{Ti}_{4.95}\text{Ta}_{0.05}\text{O}_{12}$ yields an ionic conductivity of $\sim 3 \times 10^{-8}$ S/cm. The shape of the curve and value of the ionic conductivity for $\text{Li}_4\text{Ti}_5\text{O}_{12}$ heated under air was similar to that for $\text{Li}_4\text{Ti}_{4.95}\text{Ta}_{0.05}\text{O}_{12}$. The DC electronic conductivity was $\sim 1 \times 10^{-9}$ S/cm for $\text{Li}_4\text{Ti}_{4.95}\text{Ta}_{0.05}\text{O}_{12}$ and $\sim 8 \times 10^{-10}$ S/cm for $\text{Li}_4\text{Ti}_5\text{O}_{12}$, both heat-treated under air. The electronic conductivity values for $\text{Li}_4\text{Ti}_{4.95}\text{Ta}_{0.05}\text{O}_{12}$ and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ heated under air are in close agreement. The ionic conductivity values for $\text{Li}_4\text{Ti}_{4.95}\text{Ta}_{0.05}\text{O}_{12}$ and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ of $\sim 3 \times 10^{-8}$ S/cm are in good agreement with ionic conductivity values in the literature for $\text{Li}_4\text{Ti}_5\text{O}_{12}$ heated under air by N. V. Porotnikov et al. (20) (6×10^{-8} S/cm) and S. Hayashi and H. Hatano (21) (7×10^{-8} S/cm); a factor of 3 higher than by I. A. Leonidov et al. (22) ($\sim 10^{-9}$ S/cm) and P. P. Prosini et al. (23) ($\sim 10^{-9}$ S/cm); and about an order of magnitude lower than that observed by S. Huang et al. (24) (2×10^{-7} S/cm). The DC electronic conductivity values for $\text{Li}_4\text{Ti}_{4.95}\text{Ta}_{0.05}\text{O}_{12}$ ($\sim 1 \times 10^{-9}$ S/cm) and for $\text{Li}_4\text{Ti}_5\text{O}_{12}$ ($\sim 8 \times 10^{-10}$ S/cm) heated under air are in good agreement with the results of S. Huang et al. (25), who measured $\sim 4 \times 10^{-9}$ S/cm for $\text{Li}_4\text{Ti}_5\text{O}_{12}$ heated under air. The ionic transport number (ionic conductivity/total conductivity) for $\text{Li}_4\text{Ti}_{4.95}\text{Ta}_{0.05}\text{O}_{12}$ is ~ 0.97 and for $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is ~ 0.97 heated under air. This result suggests that $\text{Li}_4\text{Ti}_{4.95}\text{Ta}_{0.05}\text{O}_{12}$ and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ when heated under oxidizing conditions are predominately ionic conductors.

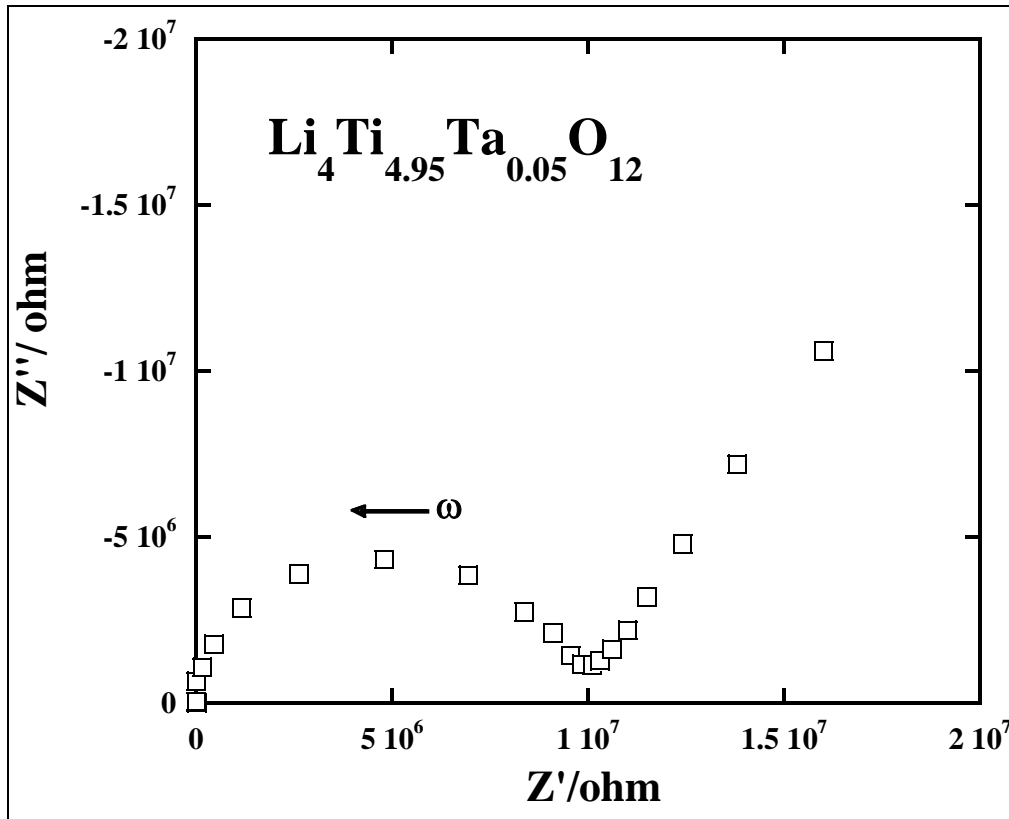


Figure 2. Complex impedance plot at room temperature of $\text{Li}_4\text{Ti}_{4.95}\text{Ta}_{0.05}\text{O}_{12}$ heated under air.

A comparison of the ionic conductivity results for $\text{Li}_4\text{Ti}_{4.95}\text{Ta}_{0.05}\text{O}_{12}$ to $\text{Li}_4\text{Ti}_5\text{O}_{12}$ heated under air can allow for a determination of the charge compensating lattice defect for Ta. According to equations 2 and 3 under oxidizing conditions, the extra charge of Ta should be compensated by a Li vacancy (equation 2) or a Ti vacancy (equation 3). For the case of compensation by a Li vacancy, an increase in ionic conductivity would be expected; whereas, for compensation by a Ti vacancy, no change in ionic conductivity would be expected. Since the ionic conductivity value of $\text{Li}_4\text{Ti}_{4.95}\text{Ta}_{0.05}\text{O}_{12}$ and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ heated under air are the same ($\sim 3 \times 10^{-8}$ S/cm), this suggests that under oxidizing conditions the extra charge of Ta is compensated by Ti vacancies rather than Li vacancies.

The complex impedance plots for $\text{Li}_4\text{Ti}_{4.95}\text{Ta}_{0.05}\text{O}_{12}$ and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ heated under reducing conditions are shown in figures 3 and 4, respectively. A comparison of figure 2 with figure 3 reveals quite a difference in the shape of the complex impedance plot exhibited by $\text{Li}_4\text{Ti}_{4.95}\text{Ta}_{0.05}\text{O}_{12}$ heated under oxidizing (figure 2) and reducing (figure 3) conditions. The complex plot for $\text{Li}_4\text{Ti}_{4.95}\text{Ta}_{0.05}\text{O}_{12}$ under reducing conditions reveals only a semicircle, suggesting a mixed ionic and electronic conductor (16, 17). The electronic conductivity determined from the low frequency intercept of the semicircle on the Z' axis yields $\sim 8 \times 10^{-4}$ S/cm. The electronic conductivity determined from DC measurements, $\sim 1 \times 10^{-3}$ S/cm, is in excellent agreement with the AC results. This is about a 10^6 increase in electronic conductivity for same material when heated under reducing conditions instead of oxidizing conditions. The high electronic conductivity value of $\text{Li}_4\text{Ti}_{4.95}\text{Ta}_{0.05}\text{O}_{12}$ for heat-treatment under reducing conditions is a result that some of the Ti^{+4} ions have been reduced to Ti^{+3} ions to compensate for the extra charge of the Ta^{+5} (equation 1), increasing the number of electrons, and hence, electronic conductivity. The electronic conductivity ($\sim 1 \times 10^{-3}$ S/cm) for 1% Ta^{+5} doped $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is in good agreement with the electronic conductivity value for 1% doping of Nb^{+5} into TiO_2 (14) ($\sim 3 \times 10^{-3}$ S/cm), where in this case a charge compensation of Nb^{+5} also occurs by the reduction of some Ti^{+4} ions into Ti^{+3} ions to increase the number of electrons, and hence, electronic conductivity.

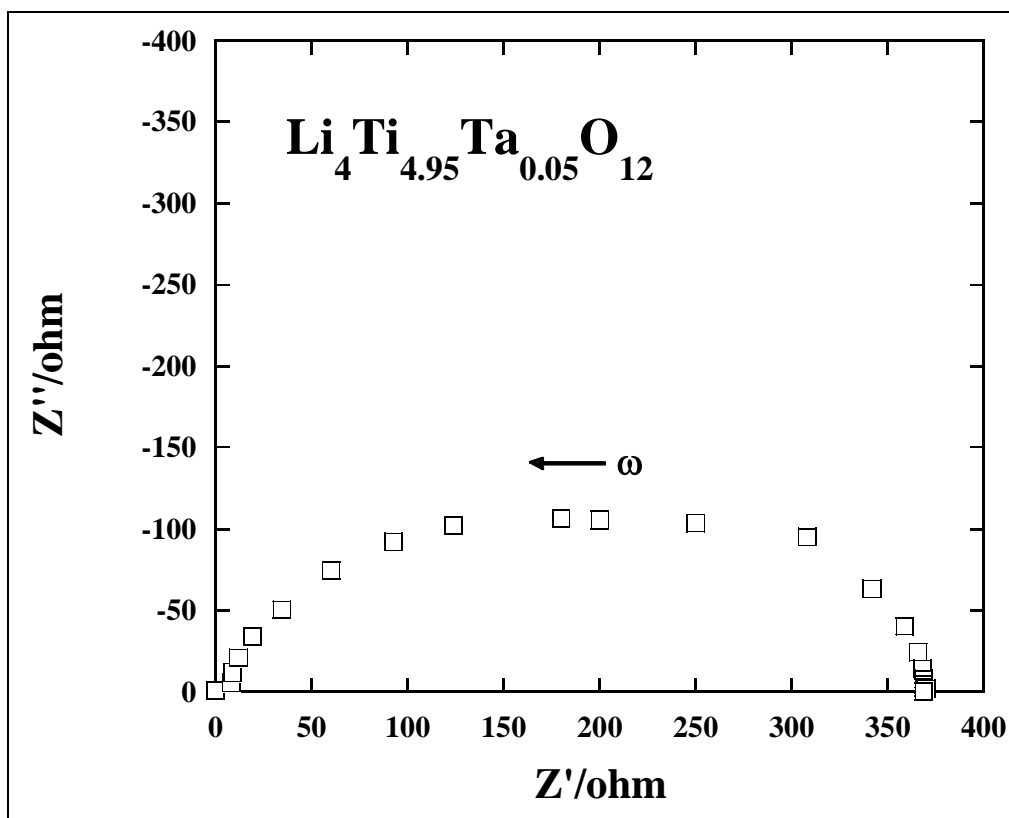


Figure 3. Complex impedance plot at room temperature of $\text{Li}_4\text{Ti}_{4.95}\text{Ta}_{0.05}\text{O}_{12}$ heated under H_2/Ar .

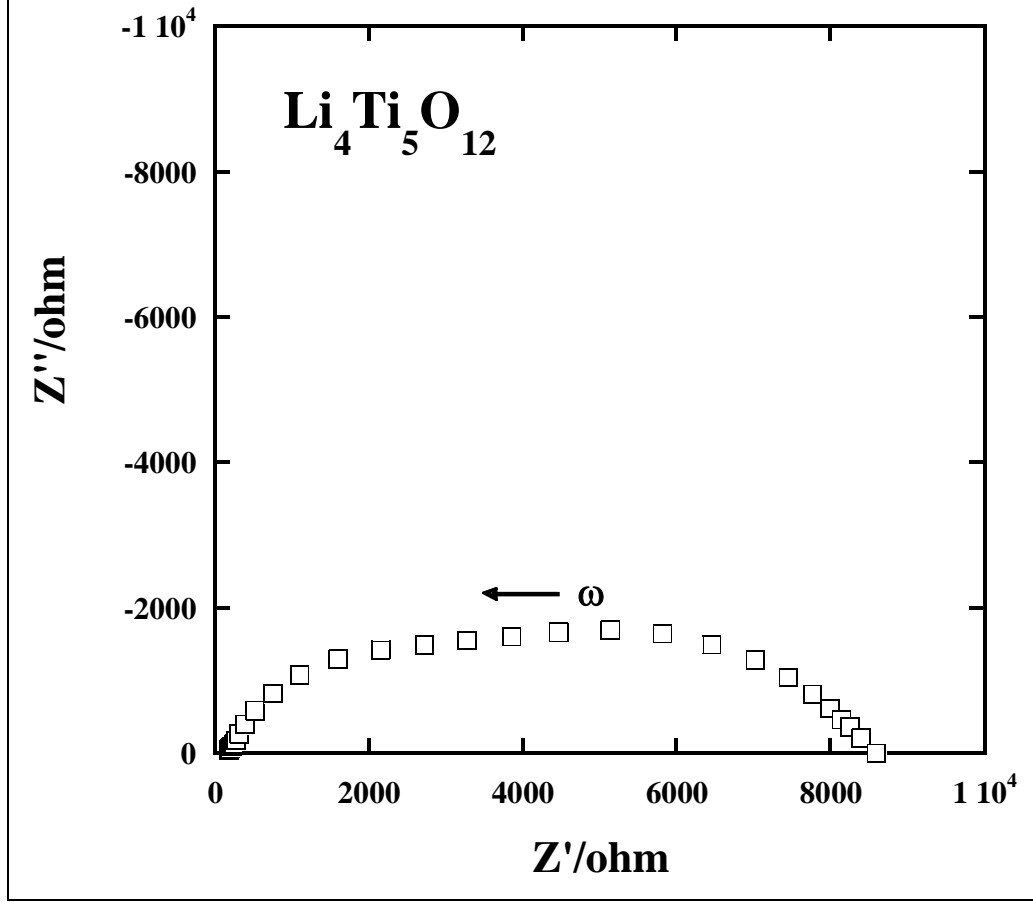


Figure 4. Complex impedance plot at room temperature of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ heated under H_2/Ar .

The electronic conductivity of Ta-doped $\text{Li}_4\text{Ti}_5\text{O}_{12}$ can also be compared to Mg-doped $\text{Li}_4\text{Ti}_5\text{O}_{12}$. The electronic conductivity ($\sim 1 \times 10^{-3} \text{ S/cm}$) for 1% Ta^{+5} doped $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (and $\text{Li}_4\text{Ti}_{4.95}\text{Ta}_{0.05}\text{O}_{12}$) is higher than for $\text{Li}_{3.95}\text{Mg}_{0.05}\text{Ti}_5\text{O}_{12}$ ($\sim 1 \times 10^{-7} \text{ S/cm}$). It would be expected in a first approximation that the electronic conductivity of these two materials to be similar, since the dopant level (i.e., the concentration of the electrons) and electron mobility for both materials should be the same. One possible reason for this difference is that at low concentrations for both the Nb and Mg materials it was observed that there is a very large change in conductivity with dopant concentration at low dopant levels (7, 14). Thus, it is possible that the dopant levels in the starting compositions (i.e., $\text{Li}_{3.95}\text{Mg}_{0.05}\text{Ti}_5\text{O}_{12}$ and $\text{Li}_4\text{Ti}_{4.95}\text{Ta}_{0.05}\text{O}_{12}$) are not the actual dopant levels, which will lead to different dopant concentrations, and hence, different electron concentrations and electronic conductivity values.

The complex plot (figure 3) for $\text{Li}_4\text{Ti}_5\text{O}_{12}$ under reducing conditions also reveals only a semicircle, suggesting a mixed ionic and electronic conductor (16, 17) similar to that for $\text{Li}_4\text{Ti}_{4.95}\text{Ta}_{0.05}\text{O}_{12}$. For the case of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ the low frequency intercept of the semicircle on the Z' axis is greater than that for $\text{Li}_4\text{Ti}_{4.95}\text{Ta}_{0.05}\text{O}_{12}$, revealing a lower electronic conductivity value. The electronic conductivity value for $\text{Li}_4\text{Ti}_5\text{O}_{12}$ determined from the low frequency intercept of

the semicircle on the Z' axis yields $\sim 4 \times 10^{-5}$ S/cm. The electronic conductivity for $\text{Li}_4\text{Ti}_5\text{O}_{12}$ determined from DC measurements $\sim 2 \times 10^{-5}$ S/cm is in good agreement with the AC results. These results are in very close agreement with the electronic conductivity results of Huang et al. (6), who observed a value of $\sim 1 \times 10^{-5}$ S/cm for $\text{Li}_4\text{Ti}_5\text{O}_{12}$ heated under a reducing atmosphere. For the case of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ unlike $\text{Li}_4\text{Ti}_{4.95}\text{Ta}_{0.05}\text{O}_{12}$, the increase in electron concentration (reduction of some Ti^{+4} ions into Ti^{+3}), and hence, the electronic conductivity results from nonstoichiometry of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ at low oxygen partial pressures (equation 4). For the case of nonstoichiometry, the charge neutrality condition is given by equation 5.



$$[\text{e}'] = 2 [\text{V}_\text{o}^{\bullet\bullet}] \quad (5)$$

where O_o^\times represents an oxygen ion and $\text{V}_\text{o}^{\bullet\bullet}$ represents an oxygen vacancy. A comparison of the electronic conductivities reveals that the electronic conductivity of $\text{Li}_4\text{Ti}_{4.95}\text{Ta}_{0.05}\text{O}_{12}$ ($\sim 1 \times 10^{-3}$ S/cm) is about 100 times higher than that for $\text{Li}_4\text{Ti}_5\text{O}_{12}$ ($\sim 3 \times 10^{-5}$ S/cm) suggesting that at the temperature, oxygen partial pressure, and dopant level used in this investigation, the electronic conductivity of the Ta-doped $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is controlled by the Ta dopant (equation 1) rather than by nonstoichiometry (equation 5).

Since, the rate is controlled by the diffusion of both the electrons and Li-ions and it is the slowest species that is controlling. Thus, increasing the rate of the one species, for example, electrons by doping, is good but not enough if this doping reduces the rate of Li-ion diffusion by hindering Li-ion motion. The results of the rate studies suggest, in order to achieve high charging and discharging rates, methods to increase the diffusivity of both electrons and ions are needed.

4. Conclusions

The effects of a 1% Ta doping level in $\text{Li}_4\text{Ti}_5\text{O}_{12}$ ($\text{Li}_4\text{Ti}_{4.95}\text{Ta}_{0.05}\text{O}_{12}$) as function of different heat-treatment atmospheres (oxidizing/reducing) was investigated to observe the effect of Ta doping on the ionic/electronic conductivity and to determine the charge compensating defects in this material. The ionic conductivity value of the white colored $\text{Li}_4\text{Ti}_{4.95}\text{Ta}_{0.05}\text{O}_{12}$ heated under an oxidizing atmosphere was $\sim 3 \times 10^{-8}$ S/cm with a DC electronic conductivity value of $\sim 1 \times 10^{-9}$ S/cm. These values are similar to values observed for $\text{Li}_4\text{Ti}_5\text{O}_{12}$ heated under the same oxidizing atmosphere. These results suggest that both materials are predominately ionic conductors, with the extra charge of Ta compensated by a lattice defect, most likely Ti vacancies. For the case of $\text{Li}_4\text{Ti}_{4.95}\text{Ta}_{0.05}\text{O}_{12}$ heated under a reducing atmosphere, it was purple colored with an electronic conductivity value of $\sim 1 \times 10^{-3}$ S/cm. $\text{Li}_4\text{Ti}_5\text{O}_{12}$ heated under a reducing atmosphere was also purple colored with an electronic conductivity value of $\sim 3 \times 10^{-5}$ S/cm. These results suggest both of these materials are predominately electronic conductors where the electronic conductivity is a result of the reduction of some Ti^{+4} ions into Ti^{+3} ions. For

$\text{Li}_4\text{Ti}_{4.95}\text{Ta}_{0.05}\text{O}_{12}$ this reduction is a result of the extra charge of the Ta; whereas, for $\text{Li}_4\text{Ti}_5\text{O}_{12}$ it is a result of nonstoichiometry. The discharge capacity of $\text{Li}_4\text{Ti}_{4.95}\text{Ta}_{0.05}\text{O}_{12}$ is lower than that for $\text{Li}_4\text{Ti}_5\text{O}_{12}$ over the entire discharge/charging region even though the electronic conductivity of the Ta-doped material has increased by a factor of 10^6 compared to the pure material. It is suggested that the poor rate capability of the doped material is as a result of Ta on the octahedral sites, through which Li must diffuse from one tetrahedral site to another tetrahedral site, hindering Li-ion diffusion, and hence, the rate capability. The results of the rate studies suggest, in order to achieve high charging and discharging rates, methods to increase the diffusivity of both the electrons and Li-ions are needed.

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Appendix. Electrical Conductivity of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ as a Function of Heat-Treatment Atmosphere

A-1 Experimental

$\text{Li}_4\text{Ti}_5\text{O}_{12}$ samples were prepared using a solid-state method from TiO_2 (rutile structure) and Li_2CO_3 . Three weight percent excess Li_2CO_3 was used to compensate for lithia volatilization during the high temperature heating. The starting materials were ground with an alumina mortar and pestle with enough methanol to form a slurry. The dried and mixed reactant mixture was pelletized and then heated at 800 °C for 12 h in air or 3 vol. % H_2/Ar . The sample was reground, pelletized, and heated for another 24 h at 800 °C in air or H_2/Ar . The $\text{Li}_4\text{Ti}_5\text{O}_{12}$ samples were first characterized by x-ray diffraction. Lattice constants were determined by fitting the data using the Rietveld refinement. To get a qualitative indication if the oxidation state of the Ti-ion varied as a function of heat-treatment atmosphere, x-ray photoelectron spectroscopy (XPS) was conducted. XPS was conducted using an Mg K_α excitation source. TiO_2 and Ti_2O_3 powders were used as reference samples. The electronic conductivity was measured on sintered and polished disk samples (~12 mm diameter and ~1 mm thickness) using the two point DC method. Ag paste electrodes were applied to the top and bottom surfaces of the disk. A high impedance multimeter was used to measure the resistance at room temperature. Conductivity was calculated from the resistance and specimen dimensions.

A-2 Results and Discussion

$\text{Li}_4\text{Ti}_5\text{O}_{12}$ samples that were heated under air were white colored; whereas, the samples heated under H_2/Ar were purple. The XRD pattern(s) of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ heated under air or H_2/Ar are shown in figure A-1. From figure A-1 it can be observed that the patterns for $\text{Li}_4\text{Ti}_5\text{O}_{12}$ heated under air or H_2/Ar are similar. They both represent a single-phase cubic material with an $\text{Fd}3\text{m}$ space group. The only difference is a slight shift in the diffraction peaks to the lower 2-theta values for the sample heated under H_2/Ar compared to under air. The lattice parameter of the air sample determined from the Rietveld analysis of the XRD pattern is $a \sim 8.356 \text{ \AA}$. This value is in good agreement with values for $\text{Li}_4\text{Ti}_5\text{O}_{12}$ prepared under an air atmosphere. The lattice parameter of the H_2/Ar sample ($a \sim 8.372 \text{ \AA}$) is slightly larger than for the air sample. A larger lattice parameter for the H_2/Ar sample compared to the air sample is expected if some of the Ti^{+4} transformed to Ti^{+3} , because of the larger size of the Ti^{+3} ion (0.81 \AA) compared to the Ti^{+4} ion (0.75 \AA). XPS of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ sample heated under air revealed that all the Ti was in the +4 oxidation state. XPS of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ sample heated under H_2/Ar revealed that some of the Ti^{+4} ions had been reduced to Ti^{+3} ions. A quantitative determination of the relative proportion of Ti^{+4} to Ti^{+3} was not determined for this report. In any case, it is important to note that the air sample had only Ti^{+4} present; whereas, the H_2/Ar sample revealed the presence of both Ti^{+4} and Ti^{+3} . The presence of the mixed $\text{Ti}^{+4}/\text{Ti}^{+3}$ valence in the H_2/Ar sample can explain the darker

color and increased lattice parameter of this sample compared to the air sample where only Ti^{+4} is present.

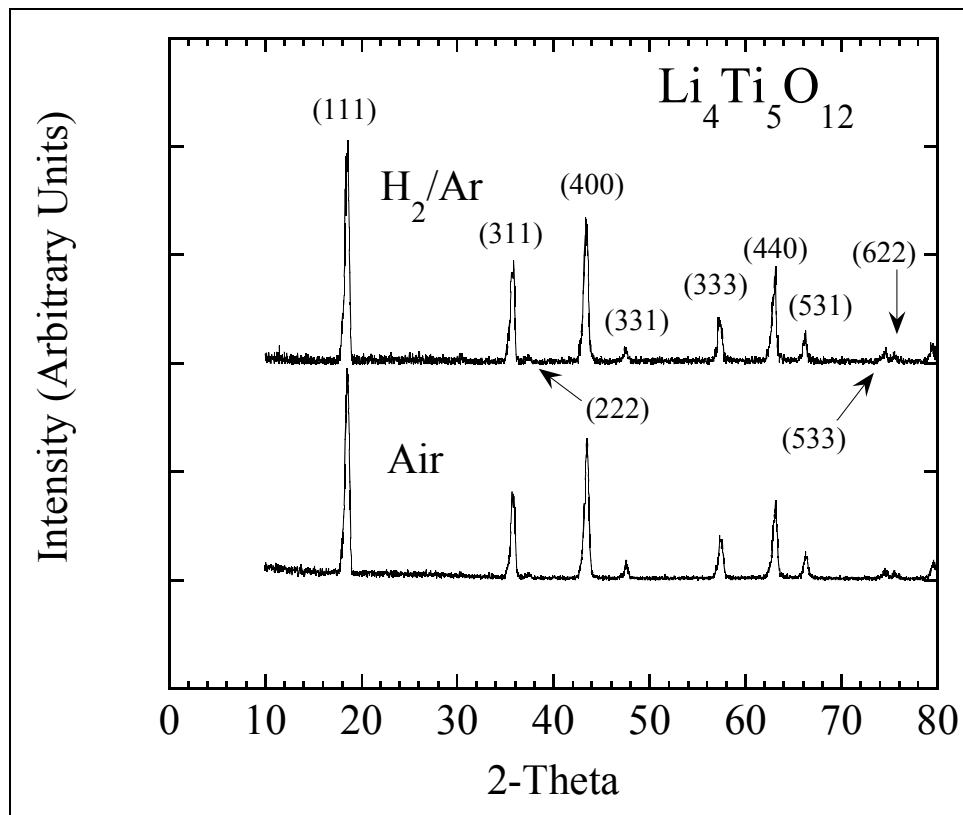


Figure A-1. XRD pattern of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ synthesized under air or 3 vol. % H_2/Ar .

It would be expected that the H_2/Ar sample would exhibit higher electronic conductivity than the air sample as a result of the mixed $\text{Ti}^{+4}/\text{Ti}^{+3}$ valence, which would lead to increased number of electrons, and hence, higher electronic conductivity. It should be noted that with our experimental setup and sample size that the lower limit of electronic conductivity that can be accurately measured is $\sim 10^{-9} \text{ S cm}^{-1}$. The electronic conductivity of the sample heated under air was below the lower limit of the experimentally measurable value. Thus, it can be concluded that the electronic conductivity of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ sample heated under air was $< 10^{-9} \text{ S cm}^{-1}$. Chen et al. (1) using the 4-point DC method suggested that the electronic conductivity of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is $< 10^{-13} \text{ S cm}^{-1}$. The electronic conductivity of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ heated under the H_2/Ar atmosphere was $\sim 1 \times 10^{-5} \text{ S cm}^{-1}$. This is an increase in electronic conductivity of at least four orders of magnitude compared to $\text{Li}_4\text{Ti}_5\text{O}_{12}$ heated under air and can be attributed to the presence of the mixed $\text{Ti}^{+4}/\text{Ti}^{+3}$ valence. Hence, it would be expected that as result of the higher electronic conductivity of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ heated under the H_2/Ar compared to under air that $\text{Li}_4\text{Ti}_5\text{O}_{12}$ heated under the H_2/Ar would exhibit a better rate-capability.

A-3 Conclusions

The results of this study reveal that there is an increase in electronic conductivity and rate-capability for $\text{Li}_4\text{Ti}_5\text{O}_{12}$ heated under a reducing atmosphere compared to heat-treatment under air. This increase is a result that during heat-treatment under the reducing atmosphere that some Ti^{+4} transformed into Ti^{+3} , leading to mixed valence Ti-ion material.

A-4 References

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